

HYDRODESULFURIZATION OF COALS

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Introduction

The Institute of Gas Technology (IGT) is engaged in a program funded by the U. S. Environmental Protection Agency (EPA) to determine the operating parameters of the primary reactors in a patented process — the IGT Flash Desulfurization Process — to desulfurize coal by a combination of chemical and thermal means. The process is directed at the production of solid fossil fuel that can be directly consumed in existing equipment in an environmentally satisfactory manner.

Laboratory, bench-scale, and continuous PDU-sized equipment are being utilized in the project. The coal sample is subjected to the selected conditions of temperature, heat-up rates and residence time in a reducing atmosphere. After treatment, the material is chemically analyzed to determine the degree of sulfur removal. Results from tests with four different, high-sulfur coals (from abundant, Eastern seams) show good sulfur reduction; calculated sulfur-dioxide emissions of the treated material are below the present Federal EPA standards of $1.2 \text{ lb}/10^6 \text{ Btu}$ for direct combustion of the solid fossil fuel product.

Coals Tested

Several coals were screened for sulfur content, seam location, and quantity available. Subbituminous coals and lignites were eliminated because of low initial sulfur content. Four bituminous coals were selected for testing:

- 1) Western Kentucky No. 9, 3.74% sulfur (run-of-mine)
- 2) Pittsburgh seam (West Virginia mine), 2.77% sulfur (highly caking)
- 3) Pittsburgh seam (Pennsylvania mine), 1.35% sulfur (high ash content)
- 4) Illinois No. 6, 2.43% sulfur (washed)

The coals were selected without regard for the relative pyritic and organic sulfur contents, because a universal coal desulfurization process should be capable of minimizing any sulfur type in the coal.

Pretreatment

The coals selected are all of the caking type and require an oxidative pretreatment prior to hydrodesulfurization. Pretreatment tests were conducted in a batch reactor to determine the proper pretreatment conditions for each coal. Temperatures, oxygen rates, fluidization velocities, and residence times were varied. These tests indicated that a temperature of 750°F and a gas velocity of 1 ft/sec were necessary. The degree of pretreatment required was not the same for each coal; residence time and oxygen consumption were adjusted to yield a non-caking material from each feedstock.

Approximately 25 to 30% of the coal sulfur is removed during pretreatment. This sulfur becomes primarily SO_2 in the low-Btu pretreatment off-gas. Approximately 8 to 12% of the coal is consumed during pretreatment, generating steam for the rest of the system and a low-Btu off-gas that can be consumed on-site to provide process steam or to generate power.

Pretreatment not only prevents caking, but also improves the sulfur removal in the subsequent hydrotreating step. Figure 1 represents two series of tests made with Western Kentucky No. 9 coal. One test series was made with crushed and screened coal and the other used crushed, screened, and pretreated coal as feed for hydrodesulfurization. The results show that the 70% sulfur removal achieved with untreated coal feed was increased to 95% by using a pretreated feed.

Hydrodesulfurization Results

Preliminary desulfurization evaluation of each coal was made in a thermobalance, a laboratory device that can continuously weigh a sample exposed to a controlled environment of temperature, pressure, and contacting gas composition. A total of 122 thermobalance tests have been performed in this program.

Samples for thermobalance tests were prepared using +40 mesh pretreated coal. This feed is placed in the sample basket and then lowered into the heated zone. Heat-up rates of 5° to 20°F per minute were used, to terminal temperatures of 1000° to 1500°F . Soaking times at the final temperature were varied from 0 minutes to 5.5 hours. The treated coal was analyzed for sulfur-by-types including pyritic, sulfide, sulfate, and organic. The small sample size did not permit more complete characterization.

Figure 2 presents the sulfur removal attained in the thermobalance tests for the four coals.

For all the coals, the pyritic sulfur has been 97 to 100% decomposed at 1300° to 1500°F , and the organic sulfur has been reduced by 80 to 88% at 1500°F . The total sulfur reduction is 90 to 95% at 1500°F . The calculated SO_2 emissions for combustion of the product, of all tests at 1400°F or above, would be below the present Federal EPA New Source Performance Standards of $1.2 \text{ lb}/10^6 \text{ Btu}$ for combustion of solid fossil fuel. If sulfide and sulfate types of sulfur are removed mechanically, all tests above 1300°F produce acceptable products.

In the tests described above, samples were heated slowly — 5° to 20°F per minute — to their terminal temperature in the thermobalance. A series of runs, with Western Kentucky No. 9 coal, employed rapid heat-up. Rapid heat-up is accomplished by heating the reaction zone to the desired temperature and then lowering the sample basket into the hot zone. Most of the total weight change occurs in the first few seconds that the sample is in the hot zone. After 15 minutes, the weight changes only slightly, regardless of the residence times. The total of sulfur removed, however, increases with residence time at rapid heat-up rate. Reduction of sulfur content by 95% has been achieved in 2 hours residence time at 1500°F ; however, samples subjected to 60 minutes or more met the EPA emission limits for SO_2 .

A batch reactor has been used with the Western Kentucky No. 9 and Illinois No. 6 coals to substantiate the results of the thermobalance and to extend testing to other phases. This reactor operates in a fluidized bed mode, similar to the anticipated operation of the full-scale plant. It can be subjected to controlled heat-up rates or can be heated rapidly. The batch reactor is capable of treating larger samples, and the treated product is completely characterized analytically. A total of 128 batch reactor tests (including pretreatment evaluation) have now been made.

Batch tests with conditions similar to the thermobalance experiments were made at terminal temperatures of 1400° and 1500°F. Results were excellent at these temperatures with the total of sulfur removed typically 90%, but as high as 98.6% at 1500°F; these results are in good agreement with the thermobalance tests. The treated material would produce SO₂ emissions well below the limitation.

Table 1 presents typical results from a batch reactor. For these tests, the product recovery is about 60%; the remainder of the coal has been gasified (and pretreated) into low-Btu gas that can be upgraded to pipeline quality or consumed on-site. The heating value of the treated product is about 5% less than the feedstock, primarily because of the lost heat-content of the coal-sulfur and the increased ash content of the product. The Volatile Matter content of the treated product has been reduced significantly; modified combustion equipment may be required for the consumption of the desulfurized coal. Alternatively, as in another IGT patent, the treated product can be recombined with the hydrocarbons produced during the treatment (after oil hydrosulfurization) to improve the combustion characteristics.

Work has now progressed to larger equipment. A 10-inch fluidized-bed unit can be fed continuously with variable feed rates from 25 to 200 lb/hr. It has been used to verify pretreatment operating conditions on a continuous basis. Pretreated feedstock has been prepared on this unit for hydrosulfurization runs which are, at the time of preparation of this paper, now planned.

This unit will be used to collect data for material and energy balances, stream characterizations, economics, and design specifications for a larger installation. We expect to have achieved positive results for oral presentation at the meeting.

Conclusions

Laboratory- and bench-scale data indicate that acceptable hydrosulfurization of coals can be achieved with the IGT Flash Desulfurization Process. Pretreatment of the coal enhances the removal of sulfur to produce a solid fuel that can be burned in conformance with the present Federal EPA limits of 1.2 lb SO₂/10⁶ Btu. Work is progressing to prove the concept on larger, continuous, PDU-sized equipment. The complete flow sheet for the process has not yet been defined, so economic factors are at present unknown.

Acknowledgement

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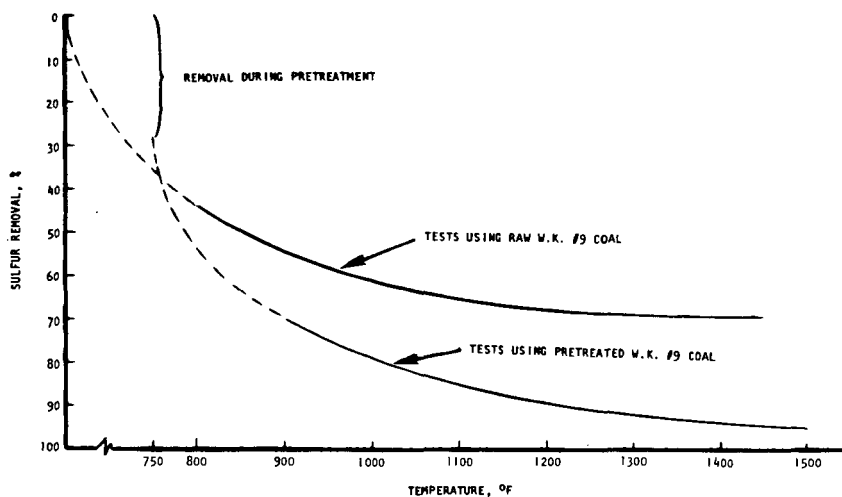


Figure 1. SULFUR REMOVAL INDICATING EFFECT OF COAL PRETREATMENT

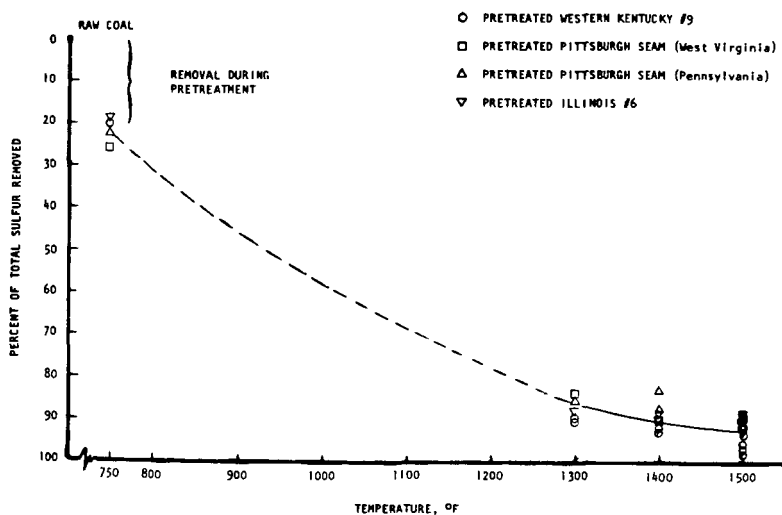


Figure 2. SULFUR REMOVAL FOR TYPICAL EASTERN COALS

Table 1. TYPICAL BATCH REACTOR RUNS

Run No.	BR-76-3			BR-76-34		
Coal Type	Run-of-Mine Western Kentucky No. 9			Washed Illinois No. 6		
Sample	Feed	Product	Feed	Product	Product	
Laboratory ID No.	26498	3196	33293	34428	1500	
Terminal Temperature, °F	1500	5	5	5	5	
Heat-Up Rate, °F/min	30	30	30	30	30	
Soaking Time, min						
Proximate Analysis, wt % (as received)						
Moisture	5.8	0.8	2.4	0.4		
Volatile Matter	36.3	3.3	34.0	3.3		
Ash	10.6	18.3	8.1	12.5		
Fixed Carbon	<u>47.3</u>	<u>77.6</u>	<u>55.5</u>	<u>83.8</u>		
Total	100.0	100.0	100.0	100.0		
Ultimate Analysis, wt % (dry basis)						
Ash	11.24	18.43	8.31	12.51		
Carbon	70.00	78.70	73.90	83.40		
Hydrogen	4.54	0.95	4.81	1.06		
Sulfur						
Sulfide	0.02	0.15	0.01	0.05		
Sulfate	0.64	0.00	0.13	0.05		
Pyritic	1.13	0.02	0.82	0.03		
Organic	<u>1.95</u>	<u>0.46</u>	<u>1.47</u>	<u>0.49</u>		
Total	3.74	0.63	2.43	0.62		
Nitrogen	1.53	0.78	1.60	0.90		
Oxygen	<u>8.95</u>	<u>0.51</u>	<u>8.95</u>	<u>1.51</u>		
Total	100.00	100.00	100.00	100.00		
Heating Value, Btu/lb	12,454	11,967	13,168	12,793		
Solids Recovery, %	62.62%	62.62%		62.70%		
Total Sulfur Removal, %	89.45	89.45		84.00		
Pyritic and Organic Sulfur Removal, %	91.96	91.96		86.58		